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STABILIZATION OF MERCURY BY SULPHUR CONCRETE: STUDY OF THE DURABILITY OF THE MATERIALS OBTAINED

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Abstract

With the aim of looking for solution for the environmental concerns of mercury a process of stabilization /encapsulation was developed under the European LIFE Program. The process consists of the obtainment of stable sulfur-concrete matrix which allows the immobilization of mercury. The final product containing up to 30% of Hg exhibits excellent mechanical properties (compressive strength >56N.mm^2 and flexural strength >8.5N.mm^2) and extremely low permeability (coefficient of water absorption by capillarity 0.07g.cm^{-2}). Physical properties as density, pore volume and porosity were also studied. The durability of these materials was analyzed in different aggressive environment, thus their behavior in alkaline medium, the ageing in salt mist environment and the resistance to freeze-thaw conditions were essayed. Any kind of degradation or deformation was observed after these tests.

Keywords: sulfur concrete, mercury stabilization, metacinnabar, mechanical properties, durability.

INTRODUCTION

The management of mercury wastes is an item that countries have focussed since some decades. It is subjected to strict health, safety and environmental legislation, especially in industrialized countries, in view of the highly toxic nature of these wastes. Mercury is considered a Priority Hazardous Substance according to European Directive 2000/60/CE, due to the adverse effects on human health and on the environment. The EU policy establishes 2011 as the cut off date for the utilization of Hg by Industry (COM/2005/0020 final, COM/2006/636 final). As a result of this, any excess of Hg should be stored in safety conditions and in safe places until definitive policies on the stabilization are available. There is therefore a need for a process that effectively stabilizes elemental Hg.

The technologies developed with the view to achieving safety dispose, aim to the immobilisation of mercury to reduce the mercury mobility towards the environment by means of stabilization [1-8] and/or encapsulation processes [9-14]. Recently, López et al. [13] and López-Delgado et al. [14] have developed a new process to stabilize/encapsulate liquid mercury by the use of a polymeric sulphur concrete. This study is a part of the European Project MERSADE (LIFE06 ENV/ES/PRE/03) for the design, construction and validation of a pilot installation for a safe deposit of mercury. On the base of this investigation, the aim of this work is to study the mechanical, physical and hydrical properties of the materials obtained, along with their behavior in different aggressive environments.

EXPERIMENTAL

Samples were prepared according to the procedure described in Patent P200930672 [13] in the form of sulphur-concrete 40x40x160mm monoliths. Mixtures of granular sulphur (type Rubber Sul 10, supplied by Repsol IPF, Madrid, Spain), gravel (< 6.3mm), siliceous sand (<4mm) and filler ($CaCO_3$, <0.125 mm) were heated at 145ºC and agitated in a mixer for 30 min. Mercuric sulphur, metacinnabar, was obtained according to López et al. [7] and incorporated into the mixture of the aggregate materials. The mass percentage of mercury in the mixture was varied between 5-30%, which corresponds to a percentage of HgS ranged between 5.8-34%. A sulphur modified polymer, STX™ [15,16] was added at the mixture which was poured into moulds and shaken in at 3000rpm for 30s. Finally, moulds were disassembled and samples were cold at room temperature. The weight of monolithic samples was around 700g. The composition of all the monoliths prepared by incorporation of metacinnabar into the sulfur-concrete is shown in Table 1. For comparison a reference sample was prepared with the same percentages of aggregate materials and sulfur but without mercury.

Table1. Composition of HgS-S-Concrete samples.

Component	Sample				
	HGS5	HGS10	HGS15	HGS20	HGS30
Gravel	23.3	21.6	19.8	18.1	14,61
Sand	46.6	43.1	39.7	36.2	29,22
Filler	7.8	7.2	6.6	6.0	4,87
S	15	15	15	15	15
HgS	5.8	11.6	17.4	23.2	34
STX	1.5	1.5	1.5	1.5	1.5

The mechanical properties such as compressive strength (S_C) and flexural strength (S_F) were measured according to the standard UNE 196-1:2005). The results were obtained as an average value of six measurements performed using a universal press Ibertest mod. Autotest 200–10–W.

The bulk (apparent) density, ρ_b, was measured by a dry flow pycnometer (GeoPyc 1360).The skeleton (relative), ρ_s, and real (absolute), ρ_r, densities were measured by He displacement Pycnometer (AccuPyc 1330). Density values were used to determine total porosity (P_T), closed porosity (P_C) and open porosity to He, according to the equations (1-3):

$$P_T\ (\%) = \left[\left(1 - \frac{\rho_b}{\rho_r}\right)\right] x\ 100 \qquad (1)$$

$$P_C(\%) = \left[\left(1 - \frac{\rho_s}{\rho_r}\right)\right] x\ 100 \qquad (2)$$

$$P_{He}(\%) = P_T - P_C \qquad (3)$$

The total pore volume was determined by the equation (4):

$$V_p = \left(\frac{1}{\rho_b} - \frac{1}{\rho_r}\right) \qquad (4)$$

To determine the water absorption by capillarity the standard UNE-EN 480 was used. Samples were set into a closed chamber (55% relative humidity) with water (5cm high) which can go up through the sample surface. At 10min, 30 min, 1h, 3h, 6h, 24h, 72h and 28 days of contact with water samples were dried with paper to remove the excess water and then weighed.

The water permeability under low pressure was determined by using the RILEM methodology (Test No. II.4) was followed, which consists of measuring the water absorbed by a surface, during a certain time, using a set of small, pipe shaped, graduated tubes, which are fixed to the wall zones to study. The quantities of absorbed water are measured through the downing of the water level observed at the tubes.

The standard UNE-EN 13580 was used to determine the water absorption and resistance to alkali for hydrophobic impregnations. The monolithic samples were set into individual 1550ml volume glasses containing a 5.6 g/l KOH solution which covered the samples. Tests were performed into a curing chamber properly conditioned. The glasses were covered with transparent film for (21±0.1) days. When this time finished the samples were dried at air until their masses were equal to initial mass ±2g. A second immersion test was carried out and the mass increasing after alkali treatment was determined ($i_{t(alk)}$). The absorption coefficient (AR_{alk}), expressed as % mass (g), was calculated by the equation (5)

$$AR_{alk} = i_{t(alk)})/\ i_1 * 100 \qquad (5)$$

where i_1 is the mass of the sample before the immersion into the alkaline solution and $i_{t(alk)}$ the mass after the second immersion.

The determination of resistance of ageing by salt mist was performed employing the standard UNE-EN 14147:2003. Samples were subjected to cycles of exposition to salt (NaCl) mist and drying in air. Tests were carried out in an accelerated ageing salt mist chamber ASCOTT Mod. 450T. The chamber temperature was held at (35 ± 5) ºC. The test consisted of 60 cycles of exposing to saline mist. A cycle consisted of 4h saline water spraying and 8h drying. Each 15 cycles the macroscopic appearance of the samples was observed to determine any kind of deformation. When the test finished samples were submerged in deionized water until the total elimination of salt (21days, water was renovated each day). Then samples were dried at 70 ± 5 ºC until constant weight (11 days).

Finally, the freeze-thaw resistance of samples was studied by the application of the standard ISO 20394:2007. Samples were subjected to 5 cycles consisting of 17 hours at -18°C, followed by 7 hours at room temperature.

RESULTS AND DISCUSSION

The appearance of the monolithic samples obtained is shown in Figure 1, in which two samples prepared with 15 and 30 % of mercury can be seen along with the reference sample.

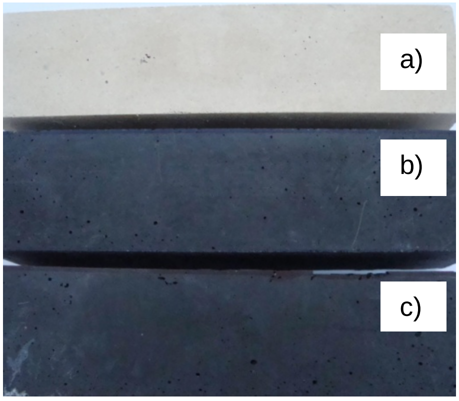

Figure1. Monolitic samples prepared by incorporation of mercury sulfide into S-concrete: a) reference, b) 15%wt Hg, c)30%wt Hg

Mechanical strength: The results of the mechanical properties, compressive strength (Cs) and flexural strength (Fs) are shown in Table 2. It can be observed a slight decreasing of both properties as the mercury content increases. But for samples with Hg content > 10% a certain tendency toward higher values is observed for both S_F and S_c. These results indicate than the polymeric matrix can incorporated high values of mercury (as HgS) without a significant modification of the mechanical properties.

Table 2. Mechanical properties: compressive strength (Cs) and flexural strength (Fs)

Sample	Fs (Mpa)	Cs (Mpa)
REF	9.6 ± 0.54	58.0 ± 2.7
SHG5	9.3 ± 0.23	56.3 ± 2.3
SHG10	8.7 ± 0.88	54.8 ± 2.8
SHG15	9.6± 1.03	55.8 ± 5.6
SHG20	9.1 ± 1.47	58.4 ± 4.2
SGH30	8.5 ± 1.17	57.2 ± 4.4

Density and Porosity: Table 3 shows the values of density, total pore volume and porosity of HgS-S-concrete obtained with 20 and 30% of mercury. An increasing of the density values (ρ_r, ρ_s and ρ_b) is observed as the Hg content increases. The porosity and the specific pore volume are smaller for samples with mercury than for reference sample. This means that metacinnabar fill the interparticle interstices and the bigger size pores (meso and macro pores) which exit in the initial S-concrete. This finding is coherent with the decreasing of total porosity and pore specific volume as the mercury content increases. The decreasing of He open porosity with the increasing of mercury fit also well with the later results

Table 3. Real (ρ_r), skeleton (ρ_s)and bulk (ρ_b) density , total pore volume (V_p) and total (P_T), close (P_C) and open (P_{He}) porosity.

Sample	REF	SHG20	SHG30
ρ_r (g/cm^3)	2.559	2.918	3.181
ρ_s (g/cm^3)	2.484	2.876	3.136
ρ_b (g/cm^3)	2.321	2.834	3.118
V_p (x10^{-2}) (cm^3/g)	3.25	1.01	0.63
P_T (%)	7.67	2.88	1.97
P_C (%)	2.93	1.44	1.40
P_{He} (%)	4.74	1.44	0.57

Water absorption by capillarity: Results of water absorption by capillarity test are shown in Table 4, in which are included the values of mass variation (ΔM) and capillary absorption (Ws) after 28 days. The water absorption by capillarity is very low for all samples, and it is even lower for HgS-S-concrete than for reference. This finding could be attributable to the fact that metacinnabar could decrease the open porosity of the concrete by filling up the external pores.

Table 4. Results of water absorption by capillarity test for samples with 20 and 30% of Hg.

Sample	Mass Variation ΔM (g)	Capillarity coefficient, W_s (g cm^{-2})
REF	2.0	0.12
HGS20	1.3	0.08
HGS30	1.2	0.07

It is worthy note that for the most building materials this test is used for no longer than 3 days. The value of capillarity for impermeable mortar ranged between 2-3 g.cm^{-2}, which is very much higher than those obtained for the mercury-sulfur-concretes.

Permeability: The essay of water permeability under low pressure was performed for 2, 5, 10, 15, 30, 60 and 180 min. The result was negative for all samples; this means that HgS-S-concretes do not absorb water by low pressure. For traditional building materials, the values of water permeability are 52mL/180min for normal mortar, 9.6mL/180 min for ceramic mortar and 1.96mL/180min for impermeable mortar. Thus it can be considered that samples of

HgS-concrete have extremely low permeability properties.

Alkali resistance: The results of test to determine the alkali absorption and alkali resistance for hydrophobic impregnation are shown in Table 5. As it can be seen the alkali absorption coefficient is very low for S-concretes obtained with 20 and 30 % of mercury; this means that these samples present a high resistance to alkali.

Table 5. Results of water absorption and alkali resistance for hydrophobic impregnation

Parameter	Sample			
	HGS20		HGS30	
	(1)	(2)	(1)	(2)
i_1 (g)	721.32	714.79	782.22	793.78
$i_{t(alk)}$ (g)	724.00	717.50	783.50	795.20
AR_{alk} (%)	0.37	0.38	0.16	0.18
Average AR_{alk} (%)	0.37		0.17	

(i_1= mass of the sample before the immersion, $i_{t(alk)}$ = mass after the second immersion, AR_{alk}= absorption coefficient)

Salt mist and freeze-thaw resistance: Concerning the tests to determine the resistance of ageing by salt mist and the resistance to freeze-thaw cycles, the results were negative, and thus samples presented a very high resistance in both aggressive environments. Cracks, surface scales or any kind of deformation or degradation were not observed in the samples after the corresponding essays.

CONCLUSIONS

The solidification/ encapsulation process developed in the patent P200930672 allows the immobilization of a high amount of liquid mercury per mass of final product (up to 30%).

The final product consists of a sulfur-concrete like material in which mercury is incorporated as metacinnabar. The HgS-S-concrete obtained exhibits excellent mechanical properties, extremely low water absorption by capillarity, very high impermeability and high durability in different aggressive environment (alkaline medium, salt mist, freeze-thaw cycles). Some of these properties are even higher than those of reference sample.

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